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ARCHIVES

COMBUSTION OF SPENT SHALE IN FLUIDIZED BED

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Large amounts of spent shale are produced during oil production from oil shale. This spent shale has a caloric value of about 1100 kcal/kg and could be used as a low grade fuel for energy production. Up to now the spent shale has not been used. The first steps towards the use of spent shale were taken by Raul Uuesoo in the fifties [1-3]. He investigated the combustion of spent shale in a fluidized bed, adapted combustion theory for spent shale particles and provided the foundation for calculations for spent shale furnaces. A part of his investigations are reported in short form in this article.

Experimental Results

The use of fuels with high ash content and low calorific value is not well suited for conventional furnaces but they can be combusted in fluidized bed. Based on this, research work on the possible burning of oil shale coke and semicoke in fluidized bed was started in 1953 at the Institute of Energetics of the Academy of Sciences of ESSR (now Estonian Energy Research Institute). The work initiated by H. H. Märtson proved the expediency of this process.

With his experimental works from 1954 to 1956 the author studied the process of burning spent shale in the fluidized bed of an experimental furnace. The tests were carried out in three different types of furnaces (Fig. 1). The cross sections of the lower part of the furnaces ranged from 0.032 to 0.036 m². The active section of grates was from 1 % to 4 %. The main target of the test bench experiments (Fig. 2) was to create conditions for maximum capture of fly ashes.

The chemical analyses of the materials used in the tests are given in the Table. The materials included coke from internal combustion vertical retorts and semicoke from tunnel retorts with outside heating.

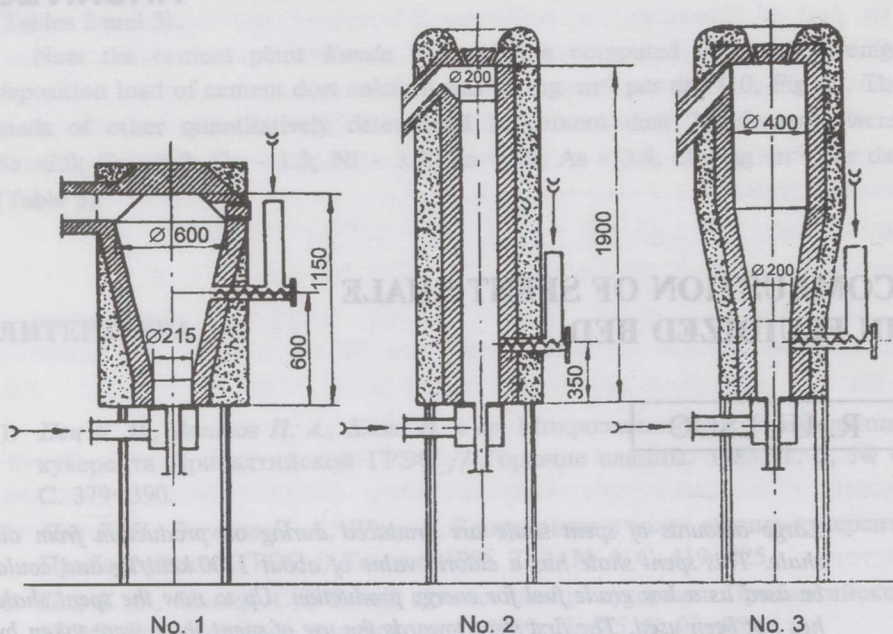


Fig. 1. Three different types of laboratory furnaces

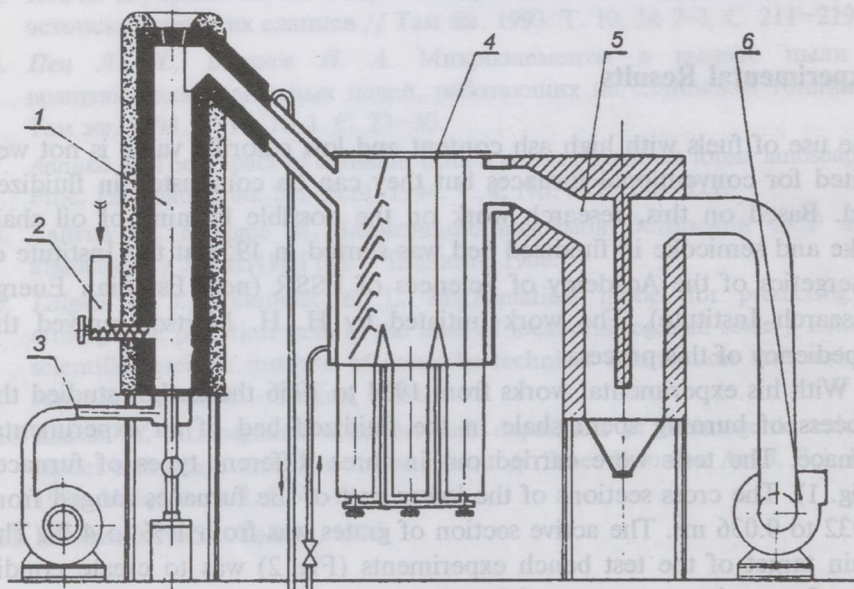


Fig. 2. Laboratory test bench: 1 - furnace, 2 - fuel hopper with fuel feeder, 3 - high pressure air fan, 4 - cooled duster, 5 - dust separator, 6 - draft fan

Chemical Analysis of Coke and Semicoke, %

Chemical Analysis (by weight)	Coke	Semicoke
Organic matter b^c	14.2–18.4	13.2
Mineral carbon dioxide $(CO_2)^d_M$	21.2–25.2	25.8
Moisture W^r	6.5–12.0	11.0

The maximum size of the fuel particles reached 3 mm. The velocity of air, calculated for the lower cross section of the furnace, varied in the range from $w_0 = 0.20$ to $0.85 \text{ m}^3/\text{m}^2\text{s}$ and the calculated coefficient of excess air α' from 1.00 to 1.55. The height of the fluidized bed was maintained between 300 and 450 mm. The specific fuel load on the cross section of the furnace remained in the range of 574 to $2600 \text{ kg}/\text{m}^2\text{h}$ and the specific volumetric heat load of the cylindrical furnace freeboard (No. 2) from 350 to $1035 \times 10^3 \text{ kcal}/\text{m}^3\text{h}$ and for the conical form (No. 3) from 90 to $235 \times 10^3 \text{ kcal}/\text{m}^3\text{h}$. The average furnace temperature ranged from 787 to $1020 \text{ }^\circ\text{C}$. A stable combustion process was achieved while burning semicoke even at a temperature of $715 \text{ }^\circ\text{C}$.

The results of the experimental research work can be summarized as follows:

(1)

The amount of combustible gases in the combustion products was insignificant. Therefore, the chemical loss with combustion products could be neglected. Mechanical losses with fly ash reached 30 %. At the same time unburned combustibles were absent in the ash from the fluidized bed.

(2)

In all the tests the maximum concentration of unburned combustibles were in the finest particles of the fly ash. The mechanical loss was highly dependent on the combustion temperature: a rise in combustion temperature from 820 to $965 \text{ }^\circ\text{C}$ lowered the mechanical loss about two times. The rate of mechanical loss was also strongly influenced by the content of organic matter in the fuel: for the combustion of oil shale semicoke the mechanical loss was over two times less than for burning oil shale coke under similar conditions. This shows that kinetic factors and fuel properties have a high influence on the combustion process, in particular at furnace temperatures below $900 \text{ }^\circ\text{C}$.

(3)

In spent shale particles the decomposition of carbonates proceeded simultaneously with burn-out of the combustible part. The decomposition process of carbonates was similar to the fuel burning process, but a higher influence of temperature was observed. The medium

decomposition rate of carbonates changed at the temperatures below 820 °C from 0.4 to 0.7. At furnace temperatures over 850 °C, the decomposition rate of carbonates remained almost constant $x_{\text{CO}_2} = 0.86-0.91$.

(4)

The velocity of air flow had a very large impact on the fuel mechanical losses and on the carbonate decomposition rate. The amount of elutriated fuel particles increased with an increase of air velocity. This also shortened the residence time of these particles in the freeboard and decreased the burn-out rate. The optimum velocity limit in experiments was $w_0 = 0.20-0.60 \text{ m}^3\text{n}/\text{m}^2\text{s}$.

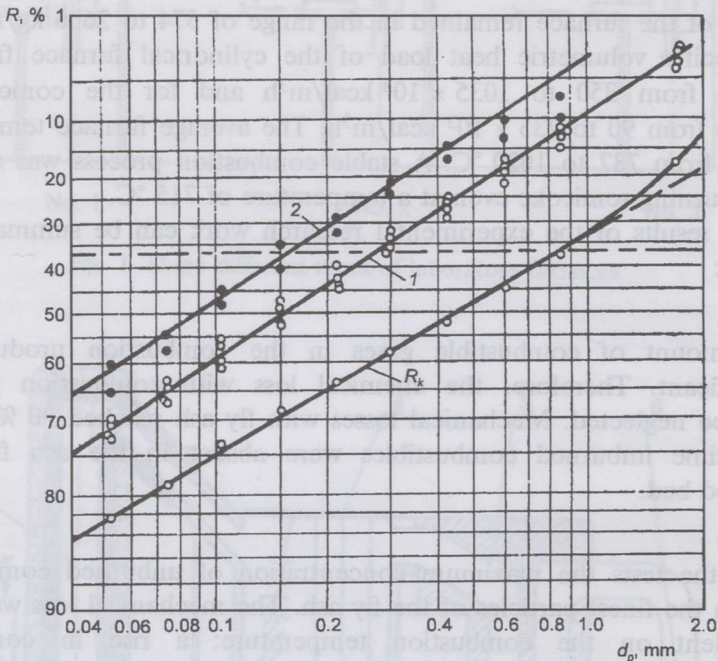


Fig. 3. The sieve characteristics of coke (curve R_k) and ash from coke burned in furnaces No.2 (curve 1) and No. 3 (curve 2)

(5)

Analyses of the flue gases along the furnace height showed that the oxygen content decreased intensively in the bottom section of the fluidized bed within 100-200 mm from the grate, but in the upper section this decrease was retarded. In some tests the oxygen content and gas temperature above the freeboard remained almost constant. This simplified the processing of test data for the burning fine particles in the furnace.

(6)

The spent shale can be considered a fuel, whose particles maintain their volume during burning, but the particles disintegrated partly in the fluidized bed furnace. This phenomenon can be explained by the mechanical wear and tear of coarse particles, which burn in the inner diffusive region.

The mechanical disintegration of particles was strongly influenced by the furnace shape and the mechanical strength of particles which in turn depended on the furnace temperature.

The screen size characteristics of coke (curve R_k) and ash from coke burning in furnace No. 2 (curve 1) and No. 3 (curve 2) are given in Fig. 3. The characteristic particle size decreased three times in the cylindrical furnace (No. 2), and up to five times in the conical furnace (No. 3).

(7)

The fluidized bed furnace could be characterized by amounts of elutriated ash and ash from fluidized bed. The furnace shape had an insignificant influence on the quantitative distribution of ashes.

The decisive factors were the air velocity and the temperature of combustion products on which was conditioned the maximum elutriated particle size of fly ash.

The fly ash elutriating from the furnace in the flue gases consisted of fine incompletely burnt fuel particles and fine dust formed from the mechanical wear of coarse particles. The fly ash also contained the particles which elutriated from the fluidized bed due to the reduced size and specific weight.

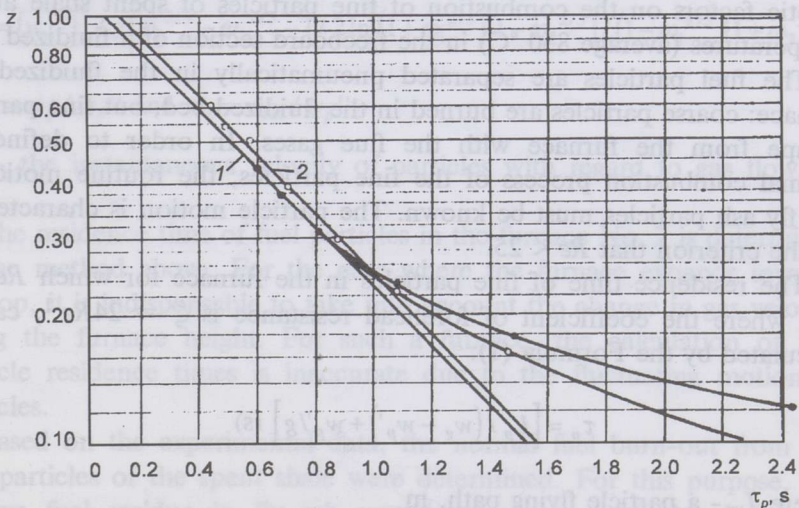


Fig. 4. The relative fuel residue in the ash particles, z , as a function of time, τ

(8)

In the furnace whose shape expanded towards the top, the fluctuating movement of ash particles could be observed. This resulted in the escape of coarser particles than would have been expected if based solely on the real velocity of flue gases in the upper section of the furnace. The fluctuating motion of the particles does not allow the determination of their residence time in the furnace and thus it is difficult to precisely calculate the combustion process.

(9)

There was an investigation of the binding properties of the ashes carried out by the Institute of Building and Building Materials of the Academy of Sciences of ESSR simultaneously with the given combustion process experimental work. This investigation showed that only fly ash produced at furnace temperatures above 850 °C could be used as a binder.

(10)

The experimental work showed that a number peculiarities of this fuel should be considered when burning Estonian spent shale. Side effects to the combustion process should also be taken into account in order to avoid incorrect conclusions.

Theory of Spent Shale Combustion

Experimental results confirm that kinetic factors have significant impact on the combustion process. Proceeding from the aforementioned research, the present work gives a profound analysis about the impact of kinetic factors on the combustion of fine particles of spent shale at low temperatures (average 850 °C) in the freeboard section of a fluidized bed.

The fuel particles are separated pneumatically in the fluidized bed furnace: coarse particles are burned in the fluidized bed, but fine particles escape from the furnace with the flue gases. In order to define the normal combustion process of the fine particles, the routine motion of the fly ash particles must be known. The particle motion is characterized by the criterion that $Re < 25$.

The residence time of fine particles in the furnace for which $Re < 1$, and where the coefficient of forehead resistance is $\zeta' = 24Re^{-1}$, can be calculated by the Formula (1):

$$\tau_p = \left[L_p / (w_g - w_p') + w_p' / g \right] \text{ (s)} \quad (1)$$

where L_p - a particle flying path, m

w_g - the real gas velocity, m/s

$w_p' = 0.545 (\gamma_p / \gamma_g v) d_p^2$ - the floating velocity of particles, m/s

The apparent specific weight of the particles, γ_p , may be considered average since the specific weight of all the particles is not homogeneous and changes within a narrow range in the burning process due to the high ash content. Multiplication of the specific weight and kinematic viscosity of the gas, $\gamma_g \nu$, depends on the composition and the temperature of the flue gases.

Calculation of the residence time for coarse particles in the furnace by traditional formulae is relatively inaccurate when the value of the criterion is $1 < Re < 25$. It became evident from the experiments that the coefficient of forehead resistance may be expressed by the following expression for all particles: $\zeta' = 20Re^{-2/3}$. Therefore, the formula of the particle floating velocity takes the following form:

$$w_p'' = 0.6775(\gamma_p / \gamma_g)^{0.75} \times (1/\nu^{0.5}) \times d_p^{1.25} \text{ (m/s)}$$

Integration of the differential equation describing the motion of particles, and taking into account the given expression for ζ'' allows one to compose relatively simple formulae for the determination of the times of particle motion. The particle flight time can be found graphically proceeding from the Formula (2):

$$L_p = w_g \tau - L_{rel} \tag{2}$$

where

$$\tau = w_p'' / g \left\{ \arctg \omega_1^{1/3} - \arctg \omega_2^{1/3} - 1/2 \ln \left[\frac{(1 + \omega_1^{1/3})(1 - \omega_2^{1/3})}{(1 - \omega_1^{1/3})(1 + \omega_2^{1/3})} \right] \right\}$$

$$L_{rel} = (w_p'')^2 / g \left\{ \omega_1^{2/3} - \omega_2^{2/3} - 1/2 \ln \left[\frac{(1 + \omega_1^{2/3})(1 - \omega_2^{2/3})}{(1 - \omega_1^{2/3})(1 + \omega_2^{2/3})} \right] \right\}$$

if $\omega_1 = w_g / w_p''$ and $\omega_2 = w_{rel} / w_p''$

w_{rel} - the instantaneous velocity of particles with regard to gas flow, m/s.

The residence time of fuel particles in the furnace No. 2 is determined by the method above. For the case where the furnace expands towards the top, it is indispensable to take into account the change in gas velocity along the furnace height. For such a furnace, the calculation of fuel particle residence times is inaccurate due to the fluctuating motion of particles.

Based on the experimental data, the normal fuel burn-out from the fine particles of the spent shale were determined. For this purpose, the relative fuel residue in fly ash particles from the cylindrical furnace (No. 2) was defined.

The processing of experimental data showed that the relationship between the relative fuel residue, z , in incompletely burned fine fuel particles, and their burning time, τ , can be precisely given in exponential form:

$$z = \exp(-AK\beta c\tau) \quad (3)$$

where $\beta = 12/32(1+\xi)$ - the stoichiometric coefficient (in this case $\xi = 0.33$)

$c = 1.429 \times 10^{-3}(T_o/T)r_{o_2}$ - the mass concentration of oxygen in the gaseous medium, g/cm³

$AK = AK_0 e^{-(E/RT)}$ - the multiplier characterizing the kinetic properties of fuels with high ash content, which is a function of temperature, cm³/g s

According to I. I. Paleyev and M. A. Gurevitch [4, 5], Formula (3) describes the combustion process in the internal kinetic region for the case where the active burning surface decreases proportionally to the fuel concentration in the particles. With this trend in the coordinates, $\tau - \log z$, the points characterizing the burning of particles in the stable medium fall along the line, independent of the particle size.

Based on the results of two tests, a diagram was drawn (Fig. 4) in order to determine the apparent AK_0 value based on the slope of straight lines. Assuming that the value of the activation energy is $E = 26900$ kcal/mol, then the average $AK_0 = 2.82 \times 10^{10}$ cm³/g s. This result is somewhat higher than that of L. A. Shilov for low temperatures $AK_0 = 1.857 \times 10^{10}$ cm³/g s [6]. This disagreement results from the different properties of spent shale used by the respective authors. The assumption that the oxygen concentration in the gaseous medium, and the temperature throughout the combustion process, were constant also added some in accuracy.

It can be concluded based on the current research results that fine particles of the spent shale are burned mainly in the internal kinetic region for the given temperature conditions. The relative fuel residue in the ash particles is calculated according to the Formula (4):

$$z = \exp(-20 \times 10^6 F\tau) \quad (4)$$

where

$$F = r_{o_2} (T_o/T) e^{-(E/RT)} \quad (5)$$

Since earlier research work had concluded that the combustion of spent shale particles in furnaces was purely diffusive burning, the results

of the present paper were repeatedly checked since the share of kinetic factors in the fine particles burning process was proven.

According to I. I. Paleyev and M. A. Gurevitch, the size of the biggest spherical particles which burn in the internal kinetic region already can be described as follows (6) [4, 5]:

$$d^k_{\max} = 2b_k \left[(D_{i0} / AK_0) e^{-(E/RT)} (T/T_0)^n (1/\gamma_b^0) \right]^{1/2} \text{ (cm)} \quad (6)$$

where $b_k = 1.5$ and $n = 1.75$.

A diagram (Fig. 5) was drawn based on Formula (6) for the determination of d^k_{\max} relative to the combustion temperature and the initial concentration of combustible material in the fuel particles γ_b^0 g/cm³. The internal diffusion coefficients for the coke from Estonian oil shale are:

$D'_{i0} = 0.029$ cm²/s - for the coke extinguished with water

$D''_{i0} = 0.062$ cm²/s - for coke not extinguished with water

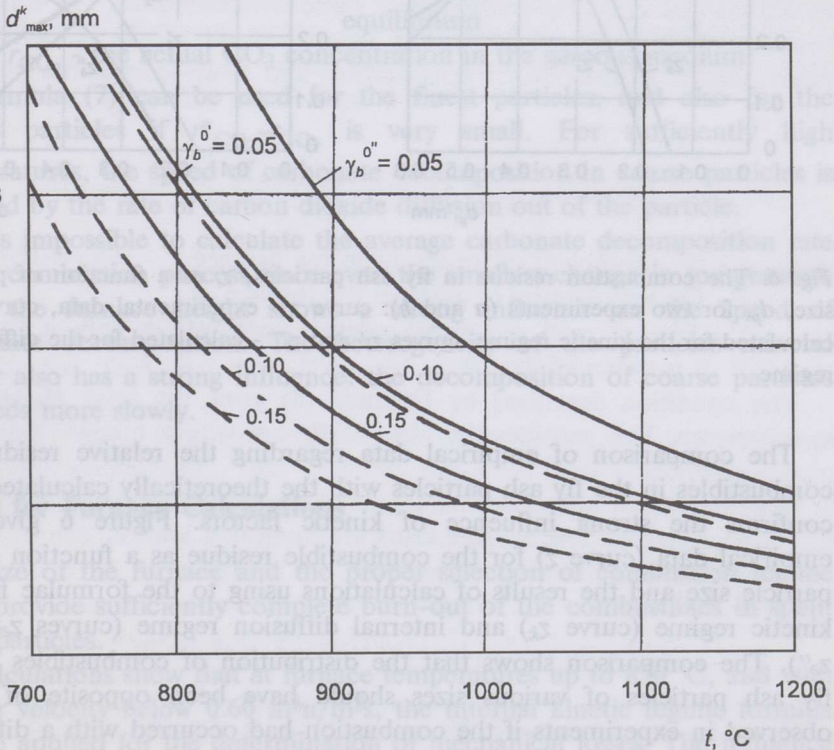


Fig. 5. Diagram for the determination of maximal particle size of coke, d^k_{\max} , as a function of the combustion temperature and initial concentration of combustibles in the fuel particles γ_b^0

Figure 5 shows that the combustion process proceeds in the internal kinetic region at relatively high temperatures even with sufficiently low concentrations of combustibles in the fine particles.

The analysis of experimental data showed that the formulae of the internal kinetic combustion yielded quite precise results, even for large particles with the diameter twice as large as d_{max}^k from Fig. 5. This results from a high kinetic resistance value in the beginning transition region of the combustion process. The asymmetrical form of the particles has an impact in the same direction.

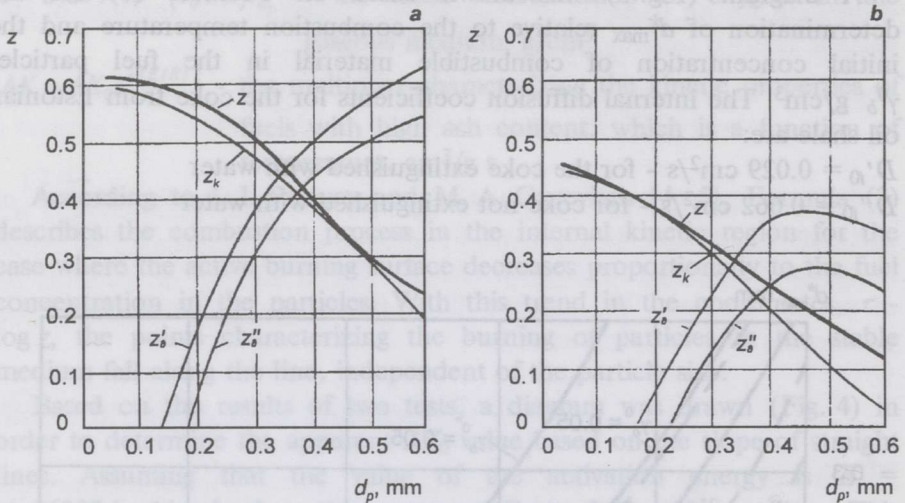


Fig. 6. The combustion residue in fly ash particles, z , as a function of particle size, d_p , for two experiments (a and b): curve z - experimental data, curve z_k - calculated for the kinetic regime, curves z_{δ}' and z_{δ}'' - calculated for the diffusional regime

The comparison of empirical data regarding the relative residues of combustibles in the fly ash particles with the theoretically calculated data confirms the strong influence of kinetic factors. Figure 6 gives the empirical data (curve z) for the combustible residue as a function of the particle size and the results of calculations using to the formulae for the kinetic regime (curve z_k) and internal diffusion regime (curves z_{δ}' and z_{δ}''). The comparison shows that the distribution of combustibles in the fly ash particles of various sizes should have been opposite of those observed in experiments if the combustion had occurred with a diffusion limiting regime.

The analysis proves that the combustion of fine particles at temperatures below 1000 °C is completely determined by kinetics factors and reactive properties of the fuel.

The combustion of coarse particles occurs more rapidly than the theoretical calculations of diffusive on-limiting combustion of spherical particles would predict. The discrepancy is evidently due to the heterogeneity of particles and the decrease of particle size resulting from particle disintegration in the furnace.

Decomposition of Carbonates in Spent Shale Mineral Matter

The decomposition of carbonates during the combustion of fine particles of spent shale at low temperatures is analogous to the burn-out of combustibles. Although the precision of the present studies does not allow one to analyze the process in detail, the analogous processing of experimental data gives the following expression:

$$x_{CO_2} = 1 - e^{-4.8(r^*_{CO_2} - r_{CO_2})\tau} \quad (7)$$

where $r^*_{CO_2} = 32 \times 10^6 e^{-(20200/T)}$ - the CO_2 concentration for the reaction equilibrium

r_{CO_2} - the actual CO_2 concentration in the gaseous medium

Formula (7) can be used for the finest particles, and also for the coarse particles if $r^*_{CO_2} - r_{CO_2}$ is very small. For sufficiently high temperatures, the speed of carbonate decomposition in coarse particles is affected by the rate of carbon dioxide diffusion out of the particle.

It is impossible to calculate the average carbonate decomposition rate in the combustion process since even the smallest change in temperature along the furnace height shows a strong influence on the speed of carbonate decomposition. The heterogeneity of the particles mineral matter also has a strong influence: the decomposition of coarse particles proceeds more slowly.

Bases for Furnace Calculations

The size of the furnace and the proper selection of combustion regime must provide sufficiently complete burn-out of the combustibles in spent shale particles.

Calculations show that at furnace temperatures up to 850 °C, and with the air velocity below 0.60 m³n/m²s, the internal kinetic regime formula can be applied for the determination of mechanical losses. The influence of diffusion factors increases with a rise in temperature and with an increase of the air velocity. Therefore it is impossible to develop exact formulae which would take into account all the peculiarities of the combustion process.

In practice, the exact calculation of mechanical losses has no decisive value. For the kinetic combustion regime, the combustible residue is at a maximum value in the finest fly ash fractions. Therefore, when designing furnaces, one must consider the allowable particle combustible residue and their residence time, (which equals the flue gas residence time).

The method for determination of the process parameters is developed for the furnace with constant cross section along its height. The main characteristic is the relationship between the furnace height, H_k , and the allowed velocity of air, w_0 .

The speed of fine particle combustion depends on the fuel properties, the combustion temperature and oxygen concentration in the gaseous medium. Temperature and oxygen concentration change with the burning of a single particle. The precise definition of this change cannot be determined since it depends on several factors from the combustion process.

Generally it is possible to prove that the value F , as defined by Formula (5), changes insignificantly during the combustion process of a fine particle. Thereby, F has its lowest value at the end of the particle combustion process. Proceeding from these considerations, the following Formula (8) was developed for the determination of the main furnace parameters as a function of temperature and final combustion product content.

$$H_k / w_0 \geq 7700 \left\{ \alpha (1 + \chi)^2 / [AK_0 \beta (\alpha - 1)] (T / T_0)^2 e^{E/RT} (-\log z') \right\} \quad (8)$$

where α - the coefficient of excess air in the furnace

T - the temperature of gases in the furnace, K

z' - the allowed maximum relative combustible loss in the fine particles of fly ash

The condition described by Formula (8) gives the ratio H_k/w_0 with some reserve. This provides the yield of fly ash with a minimum organic matter content.

The velocity of air must correspond to the fractional fuel content and the furnace height. The specific cross sectional fuel load in the furnace is determined by the following expression:

$$B / F = 36 \times 10^6 w_0 / [\alpha b^p V^{0.8} (100 - q_4)] \quad (\text{kg/m}^2\text{h}) \quad (9)$$

The size of the biggest fly ash particle is described based on the routine motion of these particles:

$$d_{\max} = 0.308 [w_0 (1 + \chi) T / T_0]^{4/5} \quad (\text{mm}) \quad (10)$$

It is found, that for a sufficiently high temperature and velocity of air, the combustible content in coarse fly ash particles has a considerable influence on the mechanical loss in the combustion process due to the combustion of these particles in the internal diffusion regime. In this case it is indispensable to check the value of the relative combustible residue in ash particles with a size of $0.75 d_{\max}$.

According to the method of I. I. Paleyev and M. A. Gurevitch, the formula for dimensionless time for these particles can be written [4, 5] as:

$$\varphi = 1.75 \times 10^{-4} \left\{ (\alpha - 1) / \left[\alpha (1 + \chi)^2 d_{\max}^2 \gamma_b^0 \right] \right\} H_k / w_0 \quad (11)$$

Based on the value, φ , the relative combustible residue in these particles, z' , can be determined from the relationship where:

$$\varphi = \left[1 - (z')^{2/3} \right] / 2 - \left[(Bi_0 - 1) / Bi_0 \right] (1 - z') / 3$$

Bi_0 is determined for spherical particles with diameter of $0.75 d_{\max}$. The calculation of diffusional combustion is comparatively inaccurate due to the influence of several factors. In Formula (11) it is indispensable to take the average value of excess air rate, α , in the upper section of the furnace, where the fine particles are burned.

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From this issue (under ARCHIVES) our journal starts publishing papers on earlier oil shale research. Being published in Russian only, they have remained hitherto unknown on the international scale.

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